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Note

Synthesis of some new non-chelating bidentate ligands

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Non-chelating bidentate ligands 1,4- and 1,3-bis(imidazol-1-yl-methylene)benzenes **5** and **6** and 1,3- and 1,4-bis (benzimidazol-1-yl-methylene) benzenes **7** and **8** have been prepared by treating 1,3- and 1,4-xylene dibromides with imidazole and benzimidazole respectively. The compounds have been characterized by spectral (^{1}H NMR, ^{13}C NMR and MS) data.

The supramolecular chemistry has led to the development of various facets of chemistry, biochemistry, medicinal chemistry and physics. In more recent years a new approach involving self-assembly of non-chelating ligands around the metal ions has been developed due to their ease in synthesis and higher yields over their organic counterparts. Though such molecules have shown significant degree of substrate specificity, the slow progress of this facet of supramolecular chemistry is mainly plagued by the non-availability of appropriately designed non-chelating bidentate ligands. The literature reported ligands are invariably based upon pyridine units[1,2]. The imidazole/benzimidazole has significant role in biochemical reactions. Herein we present a simple approach for the synthesis of imidazole/benzimidazole based non-chelating ligands with *m/p* - phenylene spacers.

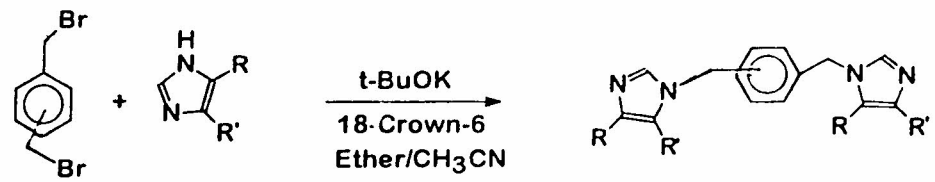
The suspension of imidazole (2.2 mole), 1,4-xylene dibromide (1.0 mole) and potassium-*t*-butoxide in dry ether containing 18-crown-6 (as catalyst) on stirring at room temperature gave 1,4-bis(imidazol-1-yl-methylene)benzene **5** in 60% yield, m.p. 74° (lit. m.p. 65-75°C)[3], m/z 238 (M^+). The structure of this compound could be assigned on the basis of the presence of one CH_2 signal at δ 5.10 (the corresponding signal is at δ 4.43 in xylene dibromide), along with imidazole and phenylene signals. Further ^{13}C NMR also corroborates this structure. In this reaction, on using two equivalents of imidazole, imidazole-1-yl-xylene bromide [m/z 250 and 252 (M^+)] remained as an impurity and could not be purified. Use of KF, KF-K_2CO_3 and K_2CO_3 as bases and tetrabutyl ammonium hydrogen sulphate as catalyst always led to a mixture of products. So the use of 10% excess of imidazole over the stoichiometric amount of dibromide and potassium-*t*-butoxide and 18-crown-6 as catalyst constitute optimum conditions for the synthesis.

Similarly, reaction of 1,3-xylene dibromide with imidazole yielded 1,3-bis(imidazol-1-yl-methylene)benzene **6** in 60% yield, m.p. 62°C, m/z 238 (M^+).

1,3- and 1,4-bis(benzimidazole-1-yl-methylene) benzenes were prepared under analogous conditions using dry CH_3CN as a solvent. **7** was obtained in 70% yield, m.p. 109°C, m/z 338 (M^+) and also **8** in 70% yield, m.p. 124°C, m/z 338 (M^+).

Experimental Section

m- And *p*-xylenes, benzoyl peroxide and N-bromosuccinimide were procured from Loba, Bombay while imidazole and benzimidazole were



1 1,3- 3 R=R'=H
2 1,4- 4 RR'=C_4H_4

5 R=R'=H
6 R=R'=H
7 RR'=C_4H_4
8 RR'=C_4H_4

purchased from Glaxo, Bombay. *m*- and *p*-xylene dibromides were prepared by the reported methods[4].

^1H and ^{13}C NMR spectra of the ligands were recorded on Bruker A.C. 200 MHz instrument using TMS as an internal reference. The +ve, –ve and absent signal pertain to the nature of signal in DEPT spectrum relative to normal ^{13}C spectrum. Mass spectra of compounds were recorded on Shimadzu GCMS OP 2000 A.

1,4-Bis(imidazol-1-yl-methylene) benzene 5. 1,4-Xylene dibromide (4 g; 0.015 mol) was rapidly added to the reaction mixture containing imidazole (2.18 g; 0.032 mole), potasium-*t*-butoxide (3.57 g; 0.032 mole) and 18-crown-6 (3-4 mg as catalyst) in dry acetonitrile. The contents were stirred for 20 h, (TLC monitored) at 25±5°C. The reaction mixture was filtered and the residue was washed twice with acetonirile. The combined filtrate was concentrated to dryness, extracted with $CHCl_3$ and treated with saline water to remove any base. The chloroform layer was dried over anhyd. Na_2SO_4, which on concentration yielded crude product of the compound which was recrystallised from $CHCl_3$-CH_3OH (1:1), yield 60%, m.p. 74°C; MS: m/z 238 (72.9, M^+), 171 (86.9, M^+–imidazole), 104 (100, M^+–2 imidazole). ^1H NMR ($CDCl_3$): δ 7.54 (s, 2H, -N=), 7.09 (dd, 4H), 7.16 (m, 4H) and 5.10 (s, 4H); ^{13}C NMR ($CDCl_3$): 50.2 (CH_2), 119.1 (CH), 127.7 (CH), 129.9 (CH), 136.4 (C), 137.2 (CH).

1,3-Bis(imidazol-1-yl-methylene)benzene 6. It was prepared by the analogous method, yield 60%, m.p. 62°C; MS: m/z 238 (55.7, M^+), 171 (55.6, M^+ –imidazole), 104 (67.9, M^+–2 imidazole), 91 (71.2, tropolium ion), 68 (100, imidazole); ^1H NMR ($CDCl_3$): δ 7.53 (s, 2H, –N=C–*H*), 7.08 (dd, 4H), 7.26 (m, 4H) and 5.10 (s, 4H); ^{13}C NMR ($CDCl_3$): 50.44 (–ve, CH_2), 119.2 (+ve, CH), 125.91 (+ve, CH), 127.12 (+ve, CH), 129.79 (+ve, CH), 130.07 (+ve, CH), 136.40 (ab, C), 137.38 (+ve, CH).

1,3-Bis(benzimidazol-1-yl-methylene) benzene 7. The mixture of benzimidazole (3.57 g; 0.03 mol), potassium-*t*-butoxide (3.57; 0.032 mol) and the catalyst 18-crown-6 (3-4 mg) was stirred in dry ether for 15 min and then *m*-xylene dibromide (4 g; 0.015 mole) quickly added. The contents were stirred for 24 h (TLC monitored) and then filtered. The residue was washed twice with ether and refluxed with acetonitrile (50 mL) for 1 h to extract the product. It was then filtered and residue washed with two portions of acetonitrile (10 mL). The combined filtrate was concentrated to half its volume which on cooling gave crystals of product. It was further purified by recrystallisation from acetonitrile, yield 70%, m.p. 109°C; MS: m/z 338 (89.1,M^+), 221 (76.9, M^+–benzimidazole), 104 (100, M^+-benzimidazole), 91 (72.5, tropolium ion); ^1H NMR ($CDCl_3$, DMSO-d_6): 7.28-7.13 (m 10H, ar-H), 8.16 (s, 2H, N=C–*H*)a, 7.69 (dd, 2H, J_1=6 Hz, J_2=2 Hz, peri-ar-H), 5.41 (s, 4H); ^{13}C NMR ($CDCl_3$, DMSO-d_6): 47.20 (-ve, CH_2), 114.01 (+ve, CH), 118.63 (+ve, CH), 120.63 (+ve, CH), 121.46 (+ve, CH), 124.71 (+ve, CH), 125.40 (+ve, CH), 128.12 (+ve, CH), 132.47 (ab, C), 135.73 (ab, C), 142.29 (ab, C), 142.50 (+ve, CH).

1,4-Bis(benzimidazol-1-yl-methylene) benzene 8. It was prepared by the analogous method, yield 70%, m.p. 124°C; MS: m/z 338 (70.5, M^+), 221 (100, M^+–benzimidazole), 104 (78.9, M^+–2-benzimidazole) and 91 (53.3, tropolium ion); ^1H NMR ($CDCl_3$, DMSO-d_6): 7.40-7.19 (m 10H, ar-H), 7.79-7.59 (m, 2H), 8.49-7.90 (m, 2H), and 5.42 (s, 4H); ^{13}C NMR ($CDCl_3$, DMSO-d_6): 45.78 (–ve, CH_2), 113.58 (+ve, CH), 117.72 (+ve, CH), 120.33 (+ve, CH), 120.95 (+ve, CH), 127.19 (+ve, CH), 135.90 (ab, C), 141.50 (+ve, CH), 142.28 (ab, C).

References

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3 The ligand **5** has been synthesized earlier (29-44% crude) by heating *p*-xylene dichloride and dry imidazole in a seated tube at 150-60°C. Schutze W & Schubert H, *J Prakt Chem*, 8, **1959**, 306; *Chem Abstr*, 54: 22596i.

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